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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

## TRANSMITTAL LETTER TO THE UNITED STATES

214468US2XPCT

DESIGNATED/ELECTED OFFICE (DO/EO/US)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

CONCERNING A FILING UNDER 35 U.S.C. 371

09/926220

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/GB00/01161

27 March 2000

26 March 1999

TITLE OF INVENTION

DETECTION OF LIQUIDS

APPLICANT(S) FOR DO/EO/US

RITCHIE Lawrence et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

## Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

**Request for Consideration of Documents Cited in International Search Report**  
**Notice of Priority**



214468US

#3/A

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

Lawrence RITCHIE ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: 09/926,220

FILED: 26 September 2001

FOR: DETECTION OF LIQUIDS :

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to a first Office Action on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please amend the claims as follows:

4. (Amended) A method according to Claim 3 wherein the hydrophobic element comprises polyvinylidene fluoride.
5. (Amended) A method according to Claim 1 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation reflected from the sensing location.

detector/analyser and output means are used to receive radiation scattered at said sensing location.

7. (Amended) A method according to Claim 1 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation transmitted through said sensing location.

8. (Amended) A method according to Claim 1 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation emitted from said sensing location.

9. (Amended) A method according to Claim 1 including a step of examining the spectroscopic characteristics of the radiation received by the detector/analyser to provide data relating to the chemical nature of liquid at the sensing location.

10. (Amended) A method according to claim 1 wherein the radiation source and detector/analyser are remote from the site and are connected to the input and output means, respectively, via waveguide means.

11. (Amended) A method according to claim 1 wherein there are a plurality of sensor assemblies which are located at different sites, and the method includes switching the connection of the radiation source and/or the detector/analyser between different sensor assemblies.

14. (Amended) An assembly according to Claim 10 wherein the detector/analyser comprises means for spectroscopic analysis.

15. (Amended) An assembly according to Claim 12 further comprising a vessel containing a hydrophobic liquid and wherein said hydrophobic element is located at a site

potentially contaminated by liquid leaking from the vessel whereby said sensor assembly is operable to detect leakage of the liquid.

16. (Amended) An assembly according to Claim 12 adapted to carry out remote monitoring by means of a telecommunication link arranged to transfer data from the sensor assembly to a remote destination.

17. (Amended) An assembly according to claim 12 wherein the radiation source and detector/analyser are adapted to be remote from the sensing location, being coupled to waveguide means for conveying radiation to and from the sensing location.

#### REMARKS

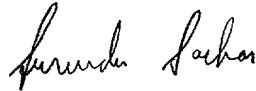
Favorable consideration of this application, as presently amended, is respectfully requested.

The present Preliminary Amendment is submitted to place the claims in more proper format under United States practice. By the present Preliminary Amendment the claims have been amended to no longer recite any improper multiple dependencies and to correct for minor informalities therein. None of the claim changes are deemed to narrow the scope of the claims.

The present application is believed to be in condition for a full and thorough examination on the merits. An early and favorable consideration of the present application is hereby respectfully requested.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Gregory J. Maier  
Attorney of Record  
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<b>Marked-Up Copy</b>
Serial No: <u>09/926,220</u>
Amendment Filed on: <u>10-17-01</u>

IN THE CLAIMS

Please amend the claims as follows:

--4. (Amended) A method according to Claim [2 or] 3 wherein the hydrophobic element [companies] comprises polyvinylidene fluoride.

5. (Amended) A method according to [any preceding] Claim 1 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation reflected from the sensing location.

6. (Amended) A method according to [any of Claims 1 to 4] Claim 1 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation scattered at said sensing location.

7. (Amended) A method according to [any of Claims 1 to 4] Claim 1 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation transmitted through said sensing location.

8. (Amended) A method according to [any of Claims 1 to 4] Claim 1 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation emitted from said sensing location.

9. (Amended) A method according to [any preceding] Claim 1 including a step of examining the spectroscopic characteristics of the radiation received by the detector/analyser to provide data relating to the chemical nature of liquid at the sensing location.

10. (Amended) A method according to [any preceding] claim 1 wherein the radiation source and detector/analyser are remote from the site and are connected to the input and output means, respectively, via waveguide means.

11. (Amended) A method according to [any preceding] claim 1 wherein there are a plurality of sensor assemblies which are located at different sites, and the method includes switching the connection of the radiation source and/or the detector/analyser between different sensor assemblies.

14. (Amended) An assembly according to Claim 10 [or 11] wherein the detector/analyser comprises means for spectroscopic analysis.

15. (Amended) An assembly according to Claim 12 further comprising a vessel containing a hydrophobic liquid and [a sensor assembly] wherein said hydrophobic element is located at a site potentially contaminated by liquid leaking from the vessel [and adapted to carry out the method of any of Claims 1 to 11] whereby said sensor assembly is operable to detect leakage of the liquid.

16. (Amended) An assembly according to Claim 12[, 13, 14 or 15] adapted to carry out remote monitoring by means of a telecommunication link arranged to transfer data from the sensor assembly to a remote destination.

17. (Amended) An assembly according to claim 12[, 13, 14, 15 or 16] wherein the radiation source and detector/analyser are adapted to be remote from the sensing location, being coupled to waveguide means for conveying radiation to and from the sensing location.--

SERIAL NO.: 09/926,220

FILED: 26 September 2001

FOR: DETECTION OF LIQUIDS

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

Sir:

Transmitted herewith is an amendment in the above-identified application.

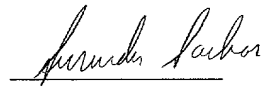
- ☐ No additional fee is required.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement previously submitted.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement submitted herewith.
- ☒ Additional documents filed herewith: PCT Transmittal Letter/Submission of Declaration/Declaration Preliminary Amendment

The fee has been calculated as shown below.

(Col. 1)		(Col. 2)		(Col. 3)	SMALL ENTITY		OTHER THAN A SMALL ENTITY	
	CLAIMS REMAINING AFTER		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
TOTAL	* 18	MINUS	** 30	= 0	X9 =	\$	X18 =	\$ .00
INDEP	* 2	MINUS	*** 3	= 0	X40 =	\$	X80 =	\$ .00
<input type="checkbox"/> FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM					+135=	\$	+270=	\$
TOTAL						\$	TOTAL	\$ .00

A check in the amount of \$\_\_\_\_\_ is attached.

- XX Please charge any additional fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.
- XX If these papers are not considered timely filed by the Patent and Trademark Office, then a petition is hereby made under 37 C.F.R. §1.136, and any additional fees required under 37 C.F.R. §1.136 for any necessary extension of time may be charged to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

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\*If the entry in Column 2 is less than the entry in Column 1 write "0" in Column 3.

\*\*If the "Highest Number Previously paid for" IN THIS SPACE is less than 20 write "20" in this space.

\*\*\*If the "Highest Number Previously paid for" IN THIS SPACE is less than 3 write "3" in this space.

Rec'd PCT/PTO 17 OCT 2001

IN RE APPLICATION OF: RITCHIE Lawrence et al.

SERIAL NO.: 09/926,220

FILED: 26 September 2001

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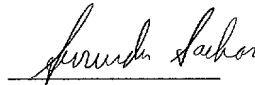
- ☐ No additional fee is required.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement previously submitted.
- ☐ Small entity status of this application under 37 C.F.R. §1.9 and §1.27 has been established by a verified statement submitted herewith.
- ☒ Additional documents filed herewith: PCT Transmittal Letter/Submission of Declaration/Declaration Preliminary Amendment

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	CLAIMS REMAINING AFTER		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
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TOTAL						\$	TOTAL	\$ .00

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- XX Please charge any additional fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.
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## DETECTION OF LIQUIDS

### Technical Field

The present invention relates to a method and apparatus for use in the detection of liquids, particularly hydrophobic liquids such as oils. It may be used for monitoring for leakage. A preferred type of embodiment employs an optical method that is capable of *detecting* and preferably *identifying* hydrocarbon liquids such as mineral or synthetic oils, petroleum, diesel, insulating oils etc. emanating from a leaking vessel, container or storage device.

A number of vessels are routinely used to carry or hold hydrocarbon solvents such as oils in a wide variety of applications. Examples include oil filled underground power cables, underground petroleum storage tanks, above surface oil containers for industrial or domestic heating, oil filled power transformers and equipment etc. Release of the container's contents, deliberate or accidental or via corrosion over time will have economic and environmental consequences. The routine monitoring of the release of oil/ solvents from these containers can be an arduous task because of the myriad of locations, distribution and varieties of such devices. A more convenient method would be one where a sensor device is placed at each container location and was able to perform continuous or periodic monitoring as required. Ideally, the sensor should be able to detect any oil/ solvent spillage as soon as it occurs in order that remedial actions can be made to minimise any ongoing loss into the environment. Such a device is referred to here as an *in-situ* sensor or monitor. Ideally, a remotely controlled sensor device that could automatically warn of oil/ solvent leakage is preferred especially where container vessels or locations are difficult to access, are widely distributed or where checks for leakage are made infrequently. Examples of such situations are discussed below.

Oil filled underground power cables

The continual supply of electrical power throughout a country relies on the integrity of underground and overhead power cables. Ease of maintenance requires that most power cables are run above ground, but where this is not possible, such as in cities, the power lines are buried some metres underground. At the operating voltages of 132 kV and above, many of the cables in service are of the oil filled type. Oil-filled cables are normally laid in sections of between 200-400 metres, which are then joined together in specially constructed joint bays. The cables and joints are then encased in a special backfill material such as speciality grade sands or cement-bound-sand (CBS).

Voids in the cable insulation can result in partial discharge activity and ultimately electrical breakdown of the cable. In an oil filled cable the oil, if maintained under sufficient pressure, prevents the formation of gaseous voids. The hydraulic system is designed to be maintained at a positive pressure at the highest points on the route profile and for this maximum static pressure at the lower points on the profile can be up to 5.25bar.

Problems arise with this type of cable when leaks appear in the pressure retaining metal jacket. Where there is a leak, the cable must be switched out if adequate pressure cannot be maintained in order to prevent the risk of electrical breakdown of the cable. The oil used in new cable installations is a synthetic mixture of alkylated benzenes, with the greatest component being dodecylbenzene (DDB). (Older cable installations employ mineral oil for insulation, but this is gradually being phased out.) Although it has not been shown to be directly carcinogenic to humans, it is of a class of chemicals (substituted benzenes) some of whom do have toxic properties, so there are environmental implications associated with leakage of this oil.

Due to the nature of the cable, leaks most often occur where two cable ends are joined, in specially constructed joint bays. Leaks in the body of the cable are much rarer, and are usually only caused by the over-zealous use of earth digging

machinery, and so are usually located immediately. Nevertheless, should a leak occur it would be detected by a fall in operating pressure over a period of time. Then the problem lies in locating in which of the many joint bays along the length of the cable the leak has sprung. Prior to this invention, detection relied on hydraulic bridge techniques, which are both time consuming and unreliable. A much-preferred method would be to install in each joint bay a device capable of providing immediate notification of a leak condition and thus ensure swift remedial measures, avoid the risk of excavating a healthy bay and minimise any disruption to power supplies.

### Underground petrol tanks

The burial of tanks containing hydrocarbon liquids has been a method of storage around the world. One of the main reasons that this method is employed is for the reduction in the risk of fire and explosion that is afforded. When sited underground the tank is protected from damage by the myriad of possible causes, and will also save on space. However, placing tanks under the ground has its own hazards. The particular problem with underground tank storage is one of tank corrosion. Whereas above ground tanks are easily inspected, underground tanks by the nature of their position are a more difficult monitoring challenge. The stability of the soil is not easily assessed, any leaks that may be occurring may continue for months or even years, and even a small leak of one drop per second may result in a loss to the soil of 400 litres per annum. Awareness of the problems has been increasing; in Britain, particularly with the Environmental Protection Act of 1990 and the Environment Act of 1995 emphasising the polluter pays principle, and increased concern over water supplies. In the USA, awareness and concern are particularly high, especially in some areas where dependence on groundwater is high. The Environmental Protection Agency estimates that 41,600,000 litres of petrol alone may be leaking from underground storage tanks every year.

A preferred route to monitoring possible leaks from underground tanks would be to install an in-situ sensor device that was buried near the tank and capable of sensing whether or not a leak had occurred, thus allowing the user to determine the integrity of the vessel on a continuous basis.

#### **In-situ monitoring devices - Prior Art**

One design for such a sensor (*TraceTek* from Raychem, USA) (see <http://www.raychem.com/products/chemelex/technology.htm> for details.) involves the two poles of an electrical switch being separated by a degradable polymer. Not only is this system expensive and difficult to install it can also produce false indications where there are low level background traces of oil, as this tends to degrade the polymer over extended periods of time.

Other methods of leak detection involve hydraulic bridge techniques. This system requires very small pressure differences to be measured and these measurements can be difficult where there are transient pressure variations and/or where cable records are unreliable and/or where there are localised thermal conditions owing for example to another heat source.

#### **Disclosure of Invention**

According to the present invention in a first aspect there is provided a method of monitoring for the presence of liquid at a site comprising: locating at said site a sensor assembly comprising a radiation source and a radiation detector and/or analyser arranged to detect and/or analyse radiation which results from the emission of radiation by the source; causing the radiation source to irradiate a sensing location; and employing said

detector/analyser to receive radiation, the arrangement being such that the nature and/or amount of radiation received by the detector/analyser is affected by the presence of liquid at the sensing location. The liquid may be a hydrophobic liquid such as oil. The sensor assembly may include a hydrophobic membrane or other element which preferentially takes up hydrophobic liquid. This affects its optical properties, e.g. reflectance of light at a membrane/glass interface. The element may be or include a fluorocarbon, e.g. polyvinylidene fluoride.

Radiation from the source interacts with the liquid in the sensing location, e.g. by one or more of reflection, absorption, transmission, scattering and fluorescence. Radiation resulting from the interaction is detected and/or analysed by the detector/analyser.

In a second aspect the invention provides an assembly comprising a vessel containing a liquid and a sensor assembly located at a site potentially contaminated by liquid leaking from the vessel and adapted to carry out the method as defined above.

In a third aspect the invention provides a sensor assembly for use in monitoring for the presence of hydrophobic liquid at a site, said assembly comprising: a hydrophobic element which is disposed so that in use it is exposed to the environment at the site and which is adapted to take up hydrophobic liquid; a radiation source arranged to irradiate at least a portion of the hydrophobic element; and a radiation detector and/or analyser arranged to receive radiation resulting from the interaction of the source's radiation with the hydrophobic element.

In a preferred type of embodiment the invention provides

an in-situ device for the detection and identification of oil or other hydrocarbon products that have leaked from vessels such as underground power cables or petrol storage tanks.

Detection of oil may be achieved by measuring the intensity of light reflected or emitted from a hydrophobic membrane at an optical window in contact with the external environment. When oil is present in the environment, it is absorbed into the hydrophobic membrane causing a change in the intensity of the reflected beam. The membrane can be one from the fluorocarbon range of membrane materials such as polyvinylidene fluoride. Identification of the oil is provided by measuring the spectral properties of the reflected beam or the spectral properties of light emanating from oil absorbed in the membrane.

In a preferred embodiment, the sensor has been designed for specific application to detecting oil leakage from underground power cables although it has clear application in other situations where oil or other hydrocarbons may leak from a vessel located underground, above ground or in water.

There may be a plurality of sensors for installation at different locations around a potential source of liquid. They may be connected via waveguides (such as fibre optics) to a detector/analyser. There may be a "multiplexing unit" such that the detector/analyser is connectable to one sensor at a time, the connected sensor being selectable and/or determined by programmed switching.

The invention can be left to operate in-situ at the monitoring site enabling convenient continuous or

periodic monitoring of the environment. Using telecommunications methods known to those skilled in the art, it is possible to transfer data from the monitoring site to a remote destination. The invention has several applications where monitoring oil or hydrocarbon leaks is required or preferred. Examples are shown in the technical description.

In the preferred embodiment, the device can be buried in sand or soil or immersed in water that surrounds an oil carrying vessel or container. If oil leaks from the vessel and contacts the sensor, it will be detected as a change in signal intensity or spectral characteristics. Such a system can therefore be used as an in-situ monitoring device that is triggered when a leak has occurred.

#### **Brief Description of Drawings**

Fig. 1 is a schematic view of apparatus used to test prototype transducers;

Fig. 2 is a circuit diagram of a prototype reflectance measurement circuit as used with the apparatus of Fig. 1; Figs. 3-6 are graphs of reflectance voltage (V) against time(s) showing responses of the prototype transducer; Fig. 7 is a view like Fig. 2 showing a modified circuit diagram;

Fig. 8 is a schematic view of apparatus used to evaluate a sensor;

Figs. 9 and 10 are graphs like Figs. 3-6 showing the response of the apparatus of Fig. 8;

Fig. 11 is a schematic view of a second form of sensor assembly in use;

Figs. 12A, B, C and D are fluorescence spectra produced using the assembly of Fig. 11; and

Fig. 13 is a schematic view of a multi-sensor device, with one sensor unit shown expanded.

## Modes for Carrying Out the Invention

### 1. Development of sensor device for monitoring cable oil leaks

One of the simplest optical measurement techniques was chosen for the sensor: the measurement of the intensity of the beam reflected from a sand surface adjacent a window. One or a number of wavelengths of light could be monitored. The presence of oil in the sand directly against a glass sensing window should cause a significant drop in the beam's reflected intensity due to absorption by the oil and diffraction occurring at the glass/oil interface. Interference in the optical signal would be caused mainly by the presence of water in the surrounding medium (which may be cement bound sand (CBS)), which to some extent would mimic the properties of oil in the sand.

Initial investigations of the optical properties of known mixtures of sand, water and cable oil were performed using an Instruments SA Fluoromax II spectrofluorimeter operating in front-face collection mode, with the sample contained within methacrylate UV fluorimetry cuvettes. the total reflectance of each of the standard mixtures was measured for different excitation wavelengths.

Five prototype sensors were built in-house for sensor characterisation. Solid state components were selected for their longevity, reliability and very low power consumption.

The apparatus is shown in Fig. 1. Its design was selected for its simplicity and ease of testing. It has a housing 8, one side of which has a glass window 10. Within the housing there is a near-IR photodiode source

12 which illuminates a surface of the window 10, which forms the sensing area of the module to be brought into contact with the sand samples 14, contained in a Petri dish 18. Light reflected from the sample window 10 is detected and measured using a near-IR phototransistor 16, also mounted in the housing. Controlled amounts of oil can be added (20) to the sand 14.

The schematic for the reflectance measurement electronics is shown in Figure 2. A photodiode D1 (e.g. SFH 409) and a first resistor R1 (e.g. 100 ohm) are in parallel with a phototransistor T1 (e.g. SD 3443) and a second resistor R2 (e.g. 1k.ohm), across a DC voltage (e.g. 5v). Current through the phototransistor, T1, is dependent on the flux of light illuminating the transistor's base electrode. The limiting resistor, R2, converts the current to an output voltage between zero and five volts.

Infrared components were chosen so that stray light would not interfere with the results (this was particularly important for tests carried out in the laboratory), and for optimum sensitivity as silicon operates most efficiently in the near IR. For simplicity, no filters were used and the total LED output was used as the excitation signal. Other sources giving rise to other wavelengths could also be used if required for a particular application. Absorption of such wavelengths could be used for the sensing mechanism especially where spectroscopic measurements (source emission or detection over a series of wavelengths) are being made. Alternatively, the fluorescence or Raman characteristics of the oil could also be measured using an alternative optical set-up. The photodiode, D1, and phototransistor, T1, were chosen for their similarities in spectral output and response.

In a further embodiment of the sensor, light from the source could be channelled along a fibre optic tube or planar waveguide. In this case, the returned light would be modified in the presence of oil. The fibre optic design is particularly relevant when distributed sensing is required as a number of fibres could be multiplexed to one sensor to cover a larger sampling area.

### 1.1 Verification of the prototype transducer

To represent the CBS that surrounds the underground cables, test samples were made by mixing dried soft building sand with water. Water is most often present in the CBS between 0% and 10% by mass. Saturation, which prevents oil from entering the sand, was found to occur for water contents approaching 30% so a maximum of 20% water was used during testing. The sand and water mixture (totalling approximately 20g) was then placed inside a plastic petri-dish which was placed upon the glass window of the sensor (as in Figure 1). Cable oil was then added dropwise to the sand mixture to simulate oil from a leaking cable encroaching upon the active sensing region. This arrangement was chosen as it permits rapid evaluation of the sensor (the oil is drawn towards the sensing window by gravity and capillary action) and it requires a minimal amount of sand and oil, so results in a minimum of waste material.

The response of the transducer to oil additions is shown in Figure 3. Oil was added to sand containing 10% water (by weight). Each arrow represents addition of 1% by weight of oil. There is clearly a drop in reflectance proportional to the amount of oil added, raising the possibility of a quantitative oil sensor. It is interesting to note the rapid sensor response time observed in the figure. It takes less than five seconds for the reflectance voltage to stabilise at a new value

after oil addition.

Because water content in the sand may exhibit wide variations, it was important to determine the extent to which this may interfere with oil measurement. Unfortunately, it was found to have a very considerable effect. Figure 4 shows the sensor output voltage (which is proportional to reflectance) as water is added to sand. Initially the sand contained 10% water and each arrow represents addition of 1% by weight of water. The response to water is similar to that for oil shown in Figure 3, effectively prohibiting the use of this method for oil detection when water content may also vary, as there is no way to differentiate between water and oil at the sensing window. Monitoring rate of change instead of absolute reflectance could be used to detect a flood of oil, since this would give a sudden change in response whereas the passage of water through the sand would be more gradual. However, we decided to develop a physical solution to the problem.

### **1.2 Improvement in selectivity and sensitivity: use of oil-selective membrane**

To remove the problem of water interference, a Fluorotrans membrane (polyvinylidene fluoride) was introduced between the sand and the sensing window. (It was placed in the petri dish 18 before the sand 14 was added.) This membrane is extremely hydrophobic, repelling water from the sensing surface while attracting organic fluids such as oil. In addition to increasing selectivity, this also increased sensitivity, as the change in reflectance of the membrane as it absorbs oil is considerably larger than that directly observed in sand.

Figure 5 shows the response obtained of the membrane-covered sensor when oil was added to the sand, each arrow indicating a 1% increase in oil concentration. The response time is significantly increased for low concentrations with respect to that achieved without the membrane, but the latency is still small with respect to the 24 hour sampling period anticipated. Figure 6 shows how insensitive the sensor response is to changes in water concentration, each arrow representing a 1% increase in water concentration.

### 1.3 Construction of prototype

Having proved the concept of the oil detection method, the method was embodied into a manufacturable sensor suitable for long term operation underground. A tube like design was used that incorporated the sensor at one end (termed the sensor head) (Fig. 8). The sensor head 30 comprises the oil detecting assembly, consisting of the reflectance measurement circuit, a glass window, a disc of *Fluorotrans* membrane and a removable glass retaining ring 32 used to keep the glass and membrane discs in place.

The reflectance measurement circuit used in this device is shown in Fig. 7. This is generally as shown in Fig. 2 and described above, except that (i) the current requirement of the circuit was reduced from 50mA to 2mA by altering the value of resistor R1 to 2k.ohm (this results in a difference in reflectance voltage with respect to that provided by the prototype sensors); and (ii) a trimmer R3 was added in series with R1 to enable the sensitivity of the transducer to be adjusted to account for any manufacturing-induced variations in the performance of the photodiode and phototransistor. The revised circuit is shown in Figure 7. The trimmer R3 may be a 100k.ohm multi-turn cermet trimmer.

The sensor device was evaluated using the experimental set-up shown in Figure 8. The large size of the device necessitated that evaluation was carried out in a much larger amount of sand 34 (500g) than that used when testing prototypes. This, coupled with the inverted nature of the transducer, resulted in slow transportation of oil to the sensing head and therefore lengthened the response time of the sensor considerably. Typically oil added to the sand surface took between 15 and 30 minutes to reach the sensing membrane. The response observed when the oil reaches the sensor surface is shown in Figure 9. Oil was added 15 minutes prior to the start of the plot.

As a precautionary measure, it was decided that a protective mesh should be added in front of the sensing membrane to prevent the possibility of sand particles tearing the membrane when the transducer is being positioned. Due to the reflective nature of the mesh, the response to oil is slightly different (see Figure 10; oil added 15 minutes prior to start of plot) but the distinction between the presence and absence of oil is still very clear.

#### 1.3.1 Long term stability tests

Additional tests were conducted to determine the integrity of the new sensor head in water and sand. These involved:

1. Leaving two transducers submerged in water for one month and checking that water did not enter the assembly or in any way affect the behaviour of the transducer.
2. Leaving two transducers buried in a beaker of sand containing 10% water for one month, then adding oil to check if the characteristic oil response was

still observed.

In both cases both transducers passed without problems.

#### **Identification of different hydrocarbons**

In order to demonstrate the detection of different types of hydrocarbon products, the sensor design was modified in order to measure the spectral characteristics of oils that were absorbed into the membrane from the environment. This was simulated in the laboratory by using a fibre optic configuration that illuminated the membrane in contact with soil and collecting the emitted light. In the presence of oil in the membrane, fluorescence emission occurs which is characteristic of each type of hydrocarbon material. The apparatus is shown in Fig. 11. The inner surface of a quartz cuvette F was lined with the fluoropolymer hydrophobic membrane G. The quartz-membrane interface represents the optical window design employed in the technical description above. The cuvette was packed with sand J to simulate the arrangement the optical-fibre sensor would take in the environment.

The optical fibre was connected to a spectrofluorimeter instrument H and synchronous scans of different fuel and oil samples were taken using the optical fibre collection system. The arrangement is shown in Figure 11. The letters in this figure refer to the following: A=lamp, B=monochromator, C=focussing lens, D=excitation fibre, E=emission fibre, F=cuvette full of sand, G=membrane.

The fluorescence excitation beam was focussed onto the membrane using a quartz lens on the end of a 25-stranded quartz fibre-optic bundle. Fluorescence collection was facilitated by another 25-stranded group of fibres co-bundled with the excitation fibres. Synchronous scans

were performed between 250nm and 500nm. Figure 12 shows the fluorescence spectra obtained from 4 different oil samples: cable oil (Fig. 12A), transformer oil (Fig. 12B), petrol (Fig. 12C) and diesel (Fig. 12D). This experimental evidence clearly shows the sensor can be used for the identification of different oils and other hydrocarbon liquids such as petroleum and diesel.

Fig. 13 shows a multi-point fibre optic sensor using the same principle of detection. A multiplicity (e.g. 10) of sensors C are each connected to a common control unit G by a respective optical cable B containing two sets of fibres - one set for transmission of light to the membrane E, the other set K for collection of light reflected or emitted from the (liquid hydrocarbons on the) membrane. The transmission and collection fibres together are referred to as a pair.

Light is channelled down a transmission fibre optic bundle J which terminates in a sensor probe head C. The sensor head employs an identical membrane to that used previously, which is illuminated by the light from the transmission optical fibres. Light reflected from the membrane surface is collected by collection fibres K in the bundle and is delivered to a detector H.

When oil is present, the intensity of the reflected light diminishes or the spectroscopic properties of the emitted light is modified owing to the presence of liquid hydrocarbons. The length of the fibre optic pair can vary (typically 1-10m in length).

A number of fibre optic pairs can be integrated by means of a single control device G. The device controls which fibre optic pair will be operated. Typically 1-10 pairs are used, and pairs may be of different length.

The control device is controlled by a microprocessor and can be controlled remotely using appropriate telecommunications.

CLAIMS

1. A method of monitoring for the presence of liquid at a site comprising: locating at said site a sensor assembly comprising radiation input means connected to a radiation source and radiation output means connected to a radiation detector and/or analyser arranged to detect and/or analyse radiation which results from the emission of radiation by the source; causing the radiation input means to irradiate a sensing location; and employing said detector/analyser to receive radiation via said radiation output means, the arrangement being such that the nature and/or amount of radiation received by the detector/analyser is affected by the presence of liquid at the sensing location.

2. A method according to Claim 1 for monitoring for the presence of hydrophobic liquid wherein the sensor assembly includes a hydrophobic element adapted to take up hydrophobic liquid from the site, and the hydrophobic element provides said sensing location.

3. A method according to Claim 2 wherein the hydrophobic element is a fluorocarbon membrane.

4. A method according to Claim 2 or 3 wherein the hydrophobic element comprises polyvinylidene fluoride.

5. A method according to any preceding Claim wherein the

radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation reflected from the sensing location.

6. A method according to any of Claims 1 to 4 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation scattered at said sensing location.

7. A method according to any of Claims 1 to 4 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation transmitted through said sensing location.

8. A method according to any of Claims 1 to 4 wherein the radiation source and input means are operated to direct radiation towards said sensing location and the detector/analyser and output means are used to receive radiation emitted from said sensing location.

9. A method according to any preceding Claim including a step of examining the spectroscopic characteristics of the radiation received by the detector/analyser to provide data relating to the chemical nature of liquid at the sensing

location.

10. A method according to any preceding claim wherein the radiation source and detector/analyser are remote from the site and are connected to the input and output means, respectively, via waveguide means.

11. A method according to any preceding claim wherein there are a plurality of sensor assemblies which are located at different sites, and the method includes switching the connection of the radiation source and/or the detector/analyser between different sensor assemblies.

12. Sensor assembly for use in monitoring for the presence of hydrophobic liquid at a site, said assembly comprising: a hydrophobic element which is disposed so that in use it is exposed to the environment at a sensing location and which is adapted to take up hydrophobic liquid; a radiation source arranged to irradiate at least a portion of the hydrophobic element; and a radiation detector and/or analyser arranged to receive radiation resulting from the interaction of the source's radiation with the hydrophobic element.

13. A sensor assembly according to Claim 12 which includes a housing containing, or coupled to, said radiation source and said radiation detector and/or analyser; said housing

having window means confronting said hydrophobic element; and said radiation source and detector/analyser being disposed or coupled so that radiation from the source can pass outwardly through the window means, and undergo reflection and/or other interaction at the hydrophobic element, interacted radiation passing inwardly through the window means to reach the detector/analyser.

14. An assembly according to Claim 10 or 11 wherein the detector/analyser comprises means for spectroscopic analysis.

15. An assembly comprising a vessel containing a liquid and a sensor assembly located at a site potentially contaminated by liquid leaking from the vessel and adapted to carry out the method of any of Claims 1 to 11 to detect leakage of the liquid.

16. An assembly according to Claim 12, 13, 14 or 15 adapted to carry out remote monitoring by means of a telecommunication link arranged to transfer data from the sensor assembly to a remote destination.

17. An assembly according to claim 12, 13, 14, 15 or 16 wherein the radiation source and detector/analyser are adapted to be remote from the sensing location, being coupled to waveguide means for conveying radiation to and from the sensing location.

18. An assembly for carrying out the method of claim 11 and comprising a detector/analyser and/or a radiation source connected to a switching unit which is connected to a plurality of sensor assemblies and is operable to switch the connection of the radiation source and/or the detector/analyser between different sensor assemblies.

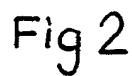


Fig3

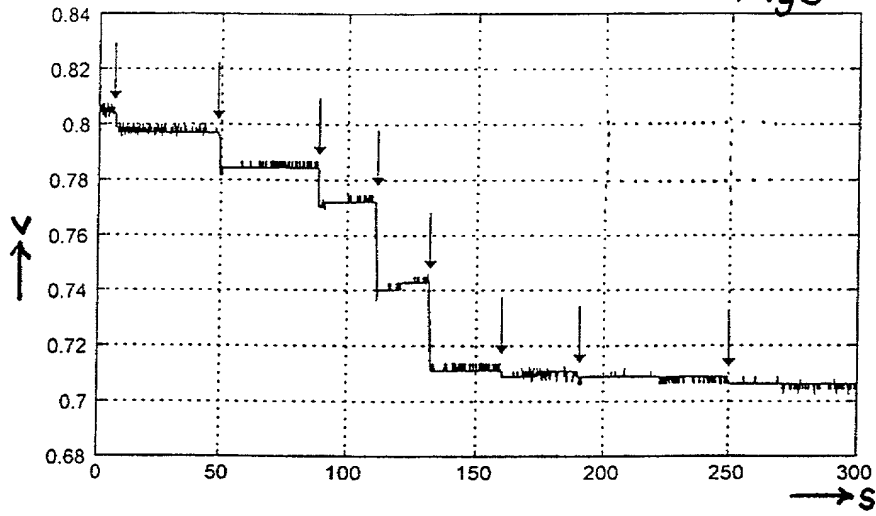


Fig4

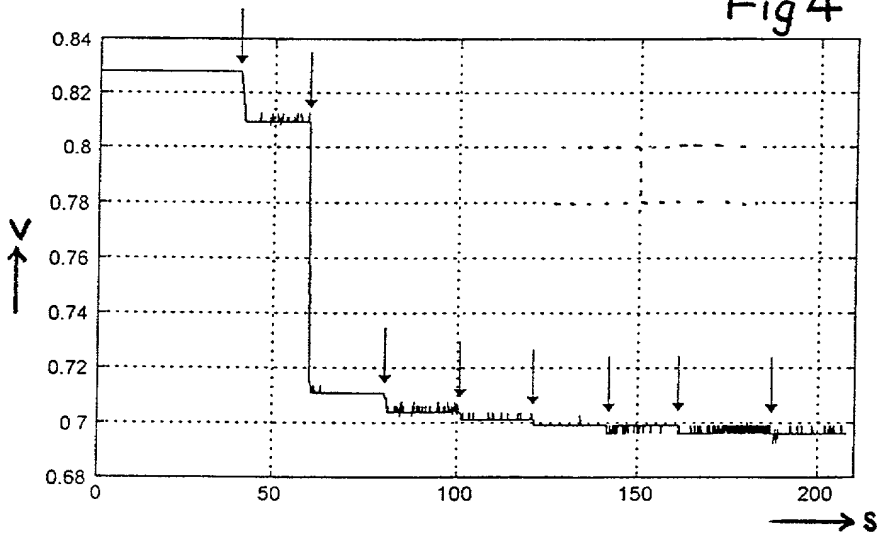


Fig 5

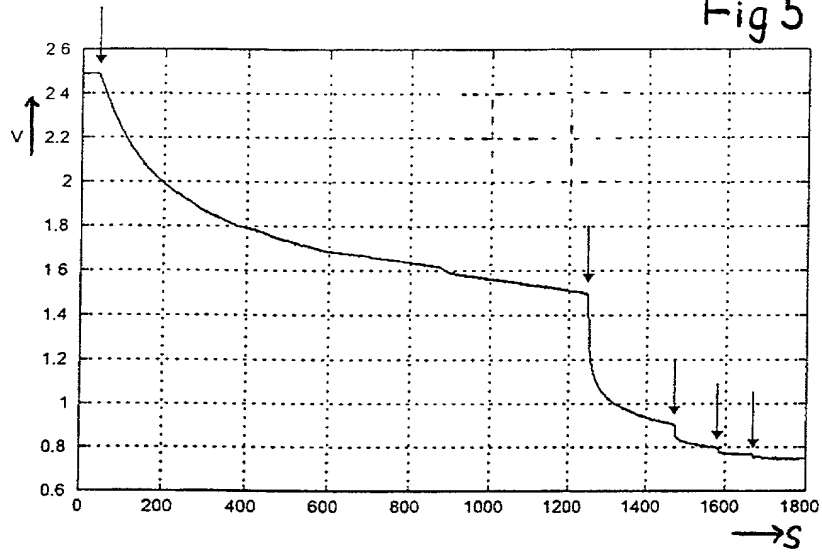


Fig 6

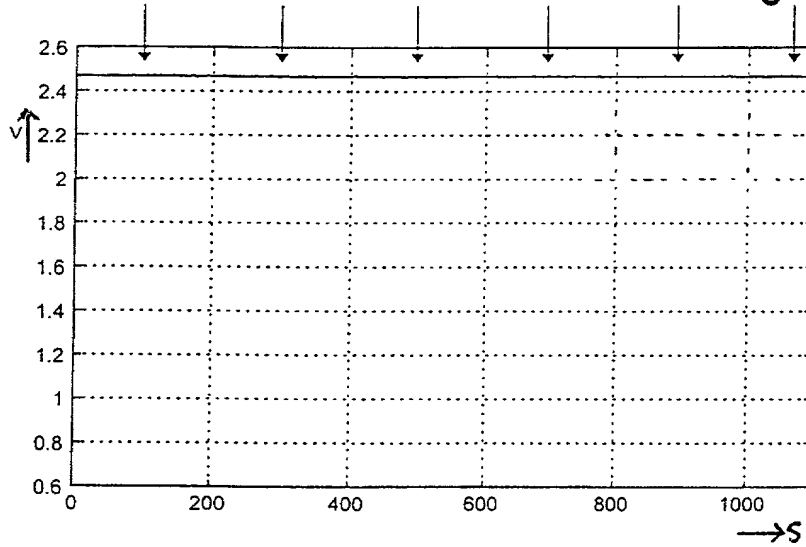


Fig 7

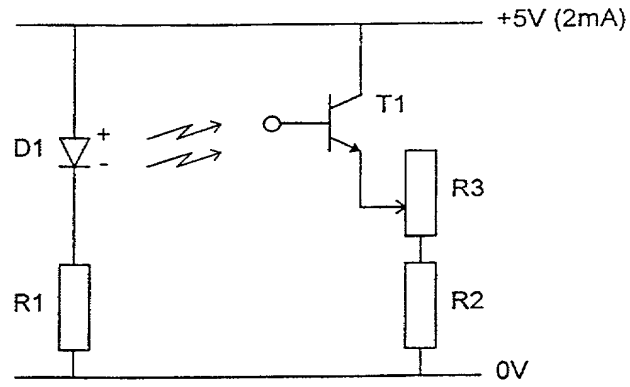


Fig 8

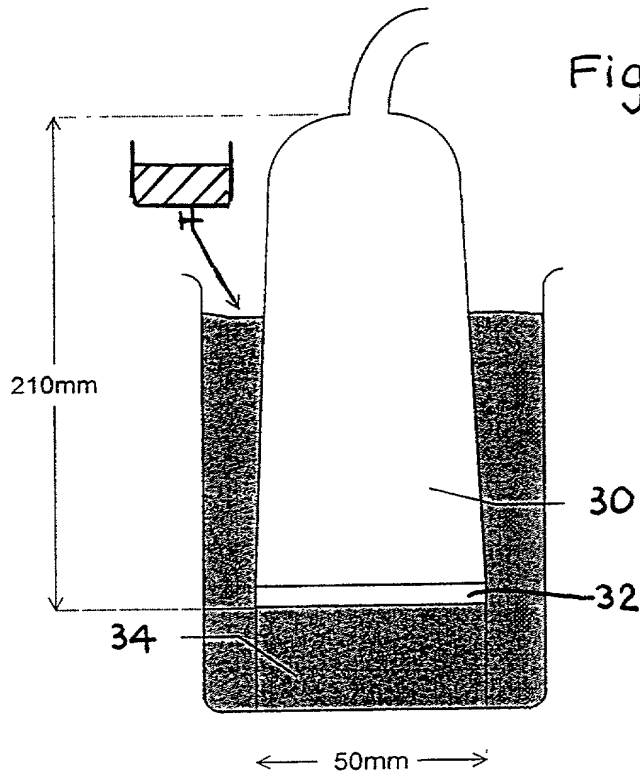


Fig 9

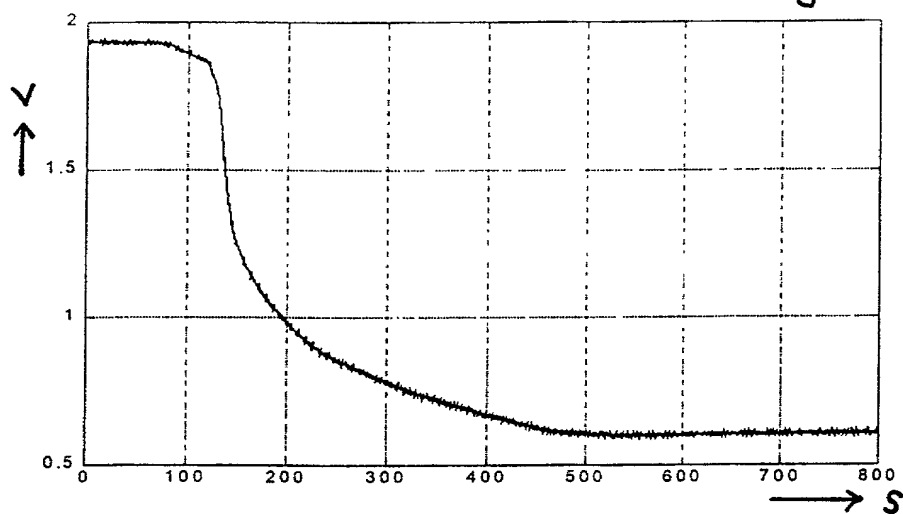
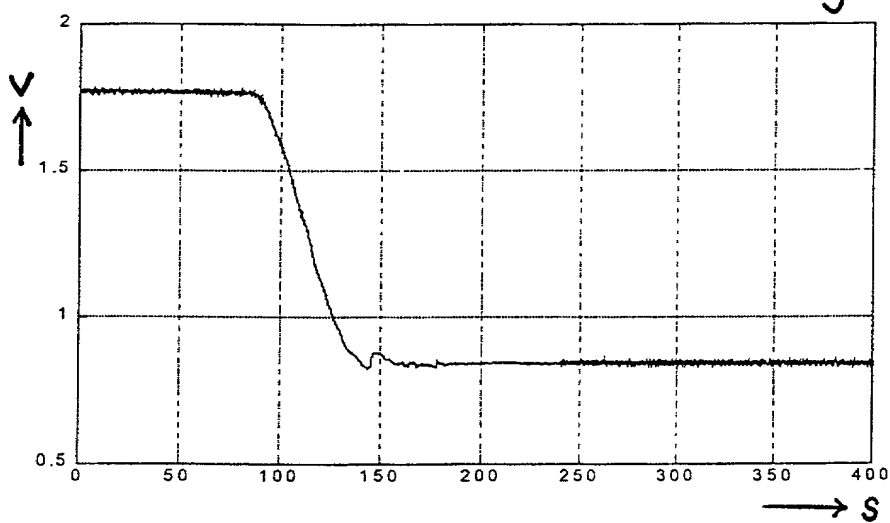
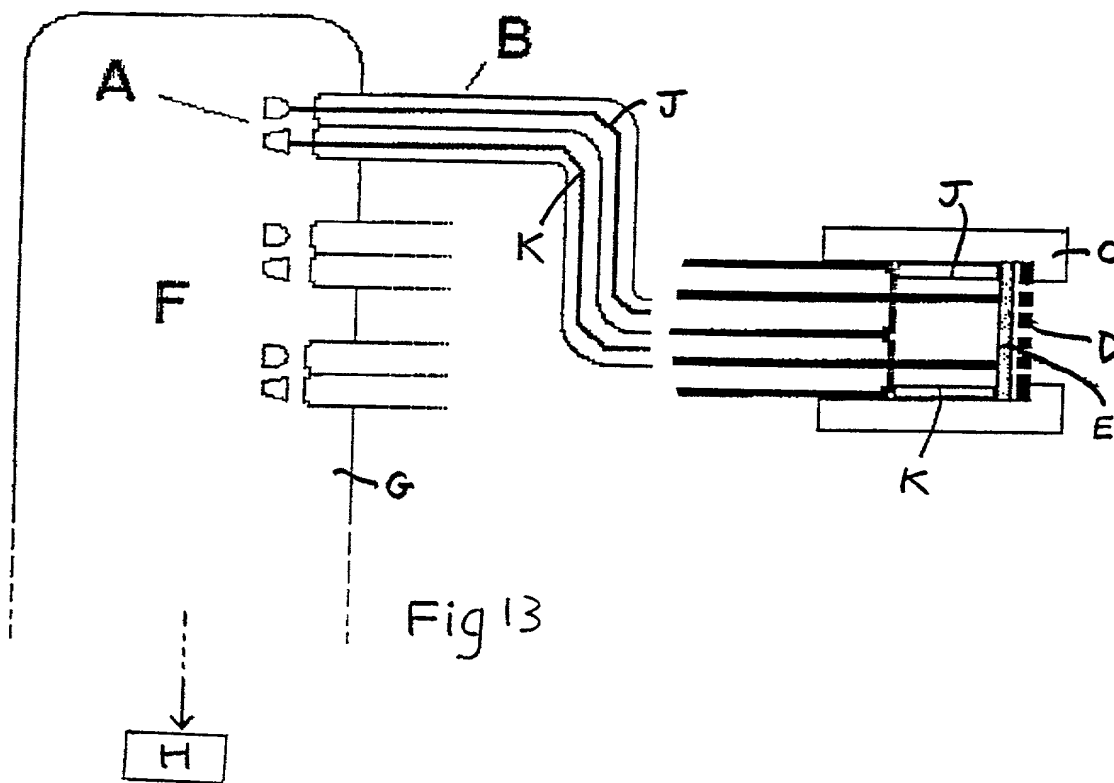
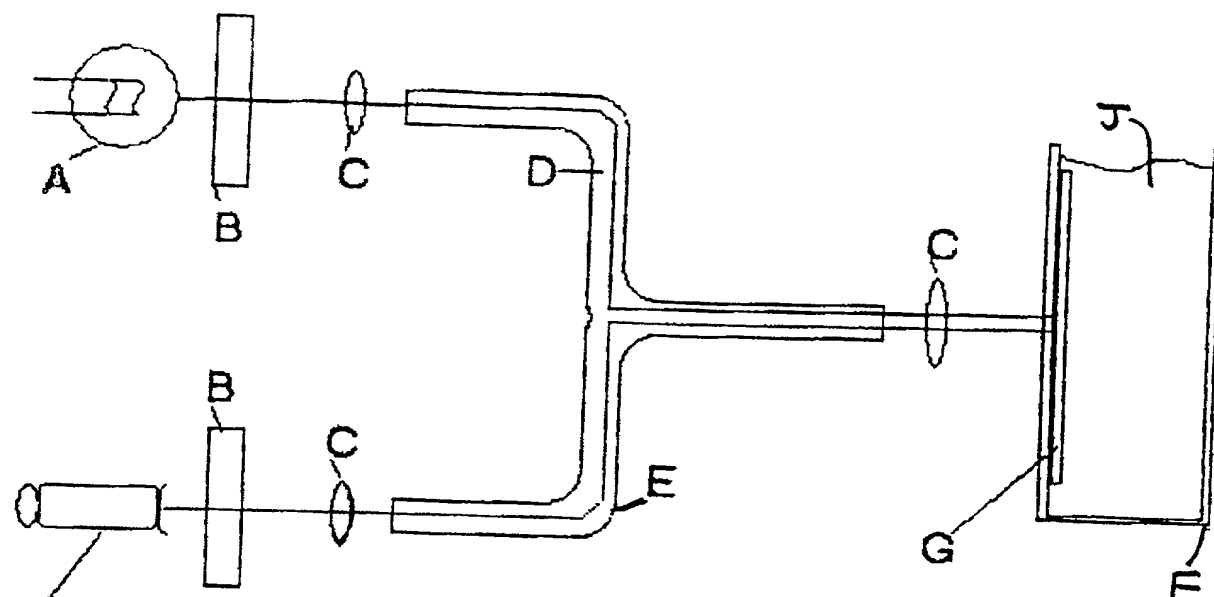
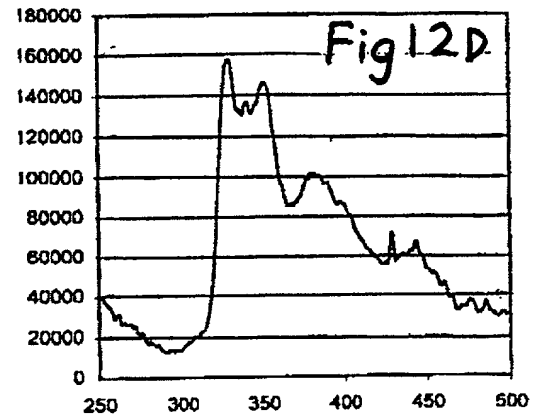
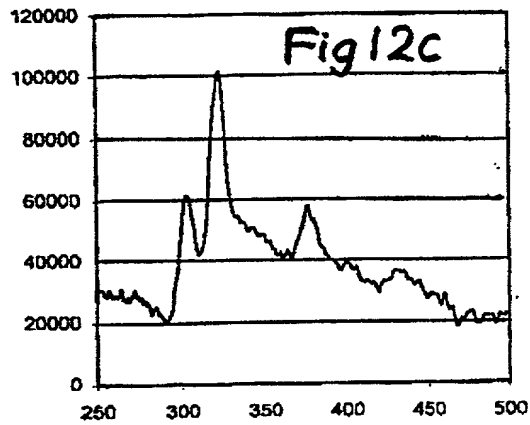
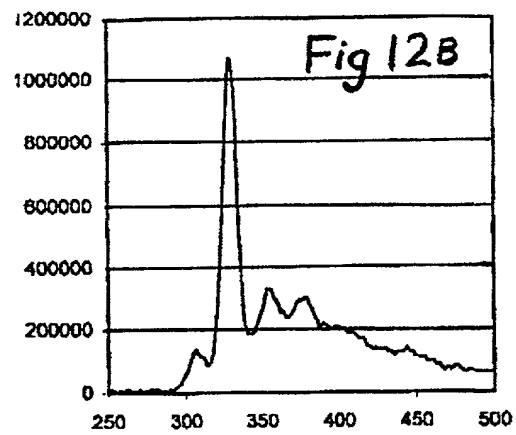
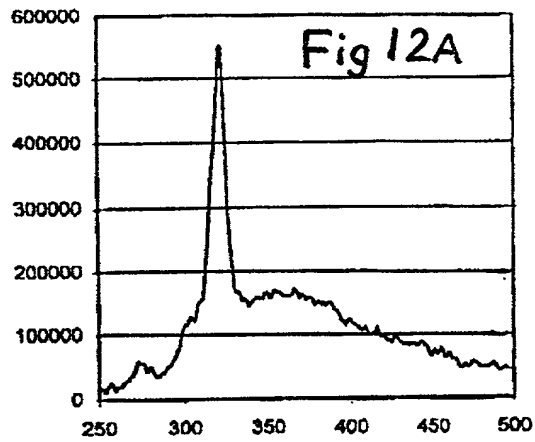


Fig 10







# Declaration, Power Of Attorney and Petition

Page 1 of 3

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Detection of Liquids

the specification of which

☐ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/GB00/01161

on 27 March 2000,

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
<u>9906949.4</u>	<u>GB</u>	<u>26 March 1999</u>	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

_____ (Application Number)	_____ (Filing Date)
_____ (Application Number)	_____ (Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint: Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; Vincent J. Sunderdick, Reg. No. 29,004; William E. Beaumont, Reg. No. 30,996; Robert F. Gnuse, Reg. No. 27,295; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Robert W. Hahl, Reg. No. 33,893; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; Paul E. Rauch, Reg. No. 38,594; William T. Enos, Reg. No. 33,128; and Michael E. McCabe, Jr., Reg. No. 37,182; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C., whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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